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REGULATION OF THE STRENGTH OF CERAMICS DURING PRODUCTION

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The mechanism of strengthening of ceramic molds is shown. Schemes for arranging the binding composition between solid components are examined. Different variants of the failure of a ceramic are shown. The great difficulties in developing analytical methods of calculating the strength of a ceramic are noted. The strength of a ceramic mold can be increased by treating it with water solutions of salts. This information will aid in choosing the optimal method of strengthening ceramic molds.

Key words: ceramic mold, ethyl silicate binder, suspension, failure, adhesion, cohesion.

Ceramic molds obtained by formation in layers on a model which subsequently is melted out of them are widely used to obtain castings comprised of heat-resistant alloys. Molds are filled at high temperatures of the metal and often in vacuum so that the molds must be of high quality. The main factors affecting the quality of a casting are the optimal bulk strength of the ceramic mold and high surface strength. Inadequate bulk strength results in failure of the mold due to the hydraulic impact of the stream of hot metal at the moment of filling. Elevated bulk strength results in the appearance of hot cracks on castings with a complex profile. Inadequate surface strength of the ceramic results in separation of refractory particles from its working surface at the time the model dissolves in water or autoclave as well as at the moment the alloy is poured into the mold, which results in the appearance of a large number of non-metallic inclusions on the surface of the cast part.

The strengthening of a ceramic mold depends on the form of the materials used, the operations performed to prepare the materials, the technology of direct formation of a ceramic envelop, melting out (dissolution) of the model and drying and firing of the ceramic.

The strengthening of a ceramic mold is due to processes associated with the formation of adhesion bonds on the interface surface between the filler and binder and cohesion strengthening of the binder itself. The character of these bonds is determined by the distribution of the binder on the surface of the refractory filler after a layer of the suspension is deposited and the layer hardens. The ethyl silicate binder used to prepare a corundum-sillimanite ceramic is the substance that promotes bonding of the filler particles in the suspension with one another. A physical-chemical analysis of the behavior of binders during their transformations is related with the situation where the failure process is of a cohesive character. A disperse powder of distensillimanite concentrate (CDSP), whose particles are nearly plate-shaped, are used as the filler in the suspension (Fig. 1). Obviously, during drying, when the binder shrinks, the sharp corners of the refractory particles are exposed. This makes it impossible to completely prevent partial adhesion failure of the strength contacts.

The process resulting in the formation of a bonding interlayer between the CDSP consists of successive stages:

1) transport stage of the formation of a contact surface between the filler and bonding component — determined by wetting and rheology processes;

2) polycondensation and mass transfer of low-molecular products of reaction;

3) weakening of the bonding of the interlayer during the dissolution of the model in water or autoclave (superheated steam);

4) solid-phase sintering during firing of the ceramic: formation of adhesion bonds on the filler – bonding component interface and cohesion strengthening of the binder itself.

Analytical methods of determining the strength involve the development of mathematical methods for determining the stress distribution in solidified films of the binder and on the boundary with the filler depending on the conditions and duration of the film formation process, the determination of the thickness of the binder film and magnitude of the adhesion and cohesion strength of the components. However, the

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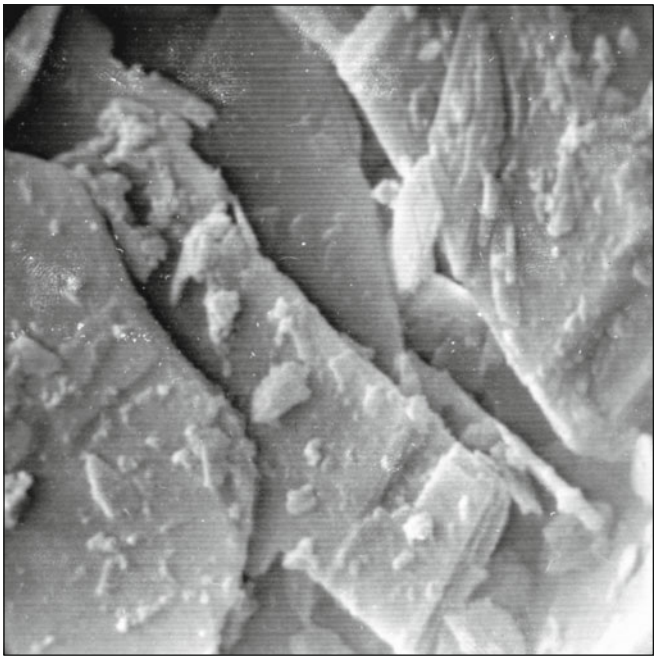

Fig. 1. Image of particles of distensillimanite concentrate (CDSP) (×3250).

existing methods are individual. The use of simplified representations and mathematical models is admissible only for approximate calculations, but their results are not applicable for determining the mechanism of hardening and softening of the binder. It is virtually impossible to take account of all factors together and to formulate a mathematical problem to determine the strength of ceramic. For this reason a number of assumptions must be made. At present, from technological standpoints the problems of determining the main directions for regulating the strength of ceramics in practice now stand at the forefront.

Some particulars of the arrangement of the solid components of ceramic should be noted. Before sprinkling powder on it the model is dipped in a suspension and the excess is allowed to run off. As the suspension runs off under gravity the flat surfaces of the CDSP particles should be oriented vertically. A dense layer of the sprinkled power grains cover the layer of the suspension, penetrating into it, and the suspension penetrates into the lower half of the sprinkled grains, wetting them, but there may not be any suspension at the locations where the sprinkled grains come into contact with one another. When the model is immersed into it the suspension is fixed more fully on the sprinkled grains.

A post-firing surface image obtained of the ceramic mold with the aid of the DRON-2 x-ray phase analyzer is displayed in Fig. 2. A large surface pore can be seen between the distensillimanite plates, oriented parallel to one another at different depths from the surface of the mold. However, in the interior layers of the mold such pores must be smaller and filled, because when the ceramic is formed in layers the suspension in the subsequent layers penetrates into the pores of the preceding layers. If the distensillimanite particles are larger than the pores, the binding solution does not enter the pores and the pores can be covered. Thus, the distribution of the binder inside and between the refractory layers can be different and is irregular.

It should be noted that the strength of a layered ceramic is formed with refractory layers whose parameters are different. For example, the viscosity of the first layer is always much higher. The impregnation of the suspension for the first layer is 2 kg CDSP per liter of the binder (hydrolyzed ethyl silicate). For subsequent layers the impregnation of the suspension is 1.2 – 1.3 kg/liter. No. 20 corundum polishing powder was sprinkled for the first layer and No. 50 powder was used for subsequent layers. This technology makes it difficult to compare analytical schemes for calculating strength.

In summary, it can be assumed that after a ceramic mold is fired the following types of contacts form between its components:

1) filler platelets which are arranged parallel to one another and are secured by a loose layer of binder;

2) grains of the sprinkled material, which secured by two layers of the suspension and are covered by the binder over the entire surface except for the surface where they touch;

3) a grain of the sprinkled material and a filler plate with a binder interlayer.

In summary, the size and shape of the binder composition affect the character of the failure of the ceramic.

The failure of a ceramic depends on the strength of single adhesion contacts between filler particles. It is possible to obtain a relation between the main parameters determining hardening and softening. The measured contact strength σ_c can be expressed as the product of the specific adhesion energy E_A and the molecular contact area S. The quantity E_A is determined by the chemical nature of the binder and filler, while S depends on the conditions of formation of the contact area and the surface state of the substrate. If defects (depressions, cracks) in which the binder flows are present on the surface, mechanical links are formed. For this reason, even if $E_A \to 0$, an adhesion contact can breakdown when such links are broken. In this case

$$\sigma_c = E_A S + P_{coh} S_{coh}, \tag{1}$$

where P_{coh} is the specific cohesion strength of the solidified binder and S_{coh} is the total area of the breaking links, determined by the surface relief of the filler.

Therefore, when links break it is necessary to take account of their attractive interaction over the cross section of the fracturing sections:

$$\sigma_c = E_A (S - S_{coh}) + P_{coh} S_{coh}. \tag{2}$$

The strength of the amorphous binder structure formed is high, but the plasticity is low. Structural defects (cracks due to internal stresses) are always present in the binding

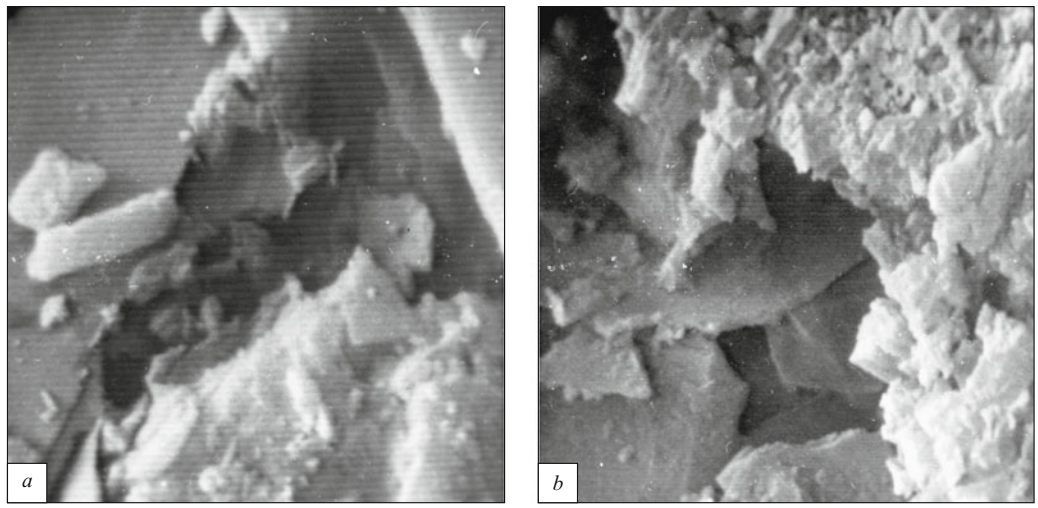

Fig. 2. Image of the surface of a ceramic mold after firing: *a*) ×6500; *b*) ×3250.

interlayer. They are formed in connection with the release of products of condensation, and during rapid solidification the breaking action of the defects increases. The drawbacks of this theory are difficulties in the theoretical or experimental determination of the strength of each type of contact. The development of a general quantitative theory of the strength of disperse systems remains problematic because of the presence of several factors that are difficult to determine: the nonunique geometry of the binding interlayers, the energy nonuniformity of the contacts, the presence of structural energy defects on the particle surfaces and internal stresses in the binding interlayers and defects in them, nonplanar (bulk) failure and others. For this reason the stresses arising must be taken into account in the expression (2):

$$\sigma_c = E_A (S - S_{coh}) + P_{coh} S_{coh} - \sigma_{in} S_1 , \qquad (3)$$

where σ_{in} represents the internal stresses and S_1 is the nominal contact area.

If $S_{coh} = 0$, no breaking of the mechanical links as a result of the links being pulled apart occurs. If $0 < S/S_1 < 1$, these links break with adhesion failure on the remaining sections of the interface. If $S_{coh}/S_1 \geq 1$ and $S_{coh} = S_1$, complete cohesion failure along the solidified binder with formation of smooth ($S_{coh}/S_1 = 1$) or rough ($S_{coh}/S_1 > 1$) breakage surfaces occurs.

If the internal stresses in the binder exceed the contact strength ($\sigma_{in} > \sigma_S$), spontaneous failure of adhesion contacts occurs and then $\sigma_S < 0$. This does not mean that E_A decreases, since σ_S is the contact strength, i.e., the stress required for the system to fail irrespective of the failure mechanism. If failure is of the cohesive character, then the measured force characterizes the strength of the weakest element of the system. For $0 < P_{coh} < E_A$, cohesion failure of strength contacts occurs irrespective of the values of S/S_1 and S_{coh}/S_1. In the opposite case adhesion failure is observed.

In summary, any character of contact failure is possible.

It is known from the literature that amorphous silica crystallizes at temperatures 1073 – 1373 K with residual porosity decreasing significantly. The centers of crystallization can be Al_2O_3 and other insoluble and nonmelting components [1], which in this case are particles of distensillimanite. In addition, the lower temperature limit corresponds to the presence of different types of crystallization centers. For mold firing temperatures 1073 – 1173 K adhesions bonds should be strengthened by the sintering of Al_2O_3 and $SiO_2 \cdot Al_2O_3$ particles with crystallizing silica. At the same time a new boundary appears inside the bonding amorphous silica — crystalline silica, which will weaken cohesion forces in the silica. Increasing the firing temperature to 1273 K and higher will weaken the cohesion bonds and soften the ceramic.

The analysis of the mechanisms of strengthening enables technological decisions directed toward changing the properties of some element of the system. This can be: modification of the bonding composition (to change the surface energy of the binder and the wetting angle of contact); cladding of the surface of the sprinkled material; increase of the contact area between filler (sprinkled material) and binder particles; increase of the cohesion strength of the binder; decrease of the internal stresses and defect density in the solidified binder. It should be noted that the mechanism of the effect on the properties of the ceramic mold during and after the mold production process are different. For example, the permeation of the finished mold by strengthening solutions only fills the open pores, but the concentration of the strengthening material can be significantly higher than in the case where it is introduced in the suspension. In the second case it is possible to change the technological properties of the suspension, for example, the coverage and rejection of ceramic molds during their production process. This limits the amount of additive introduced. However, permeation requires additional operations, just as in the case of added cladding on the sprinkled material and finer grinding of the refractory filler. It is evident that the choice of strengthening method depends on the

conditions under which the mold is obtained, the alloy poured and the chemical composition of the alloy.

Many methods of strengthening and softening exist for corundum-sillimanite ceramic produced using ethyl silicate binder. However, many of them do not permit, together with changing the strength of the ceramic to the required values, a parallel reduction of the chemical activity of the ceramic to the metallic melt. One promising direction for solving this problem is permeation of water solutions of salts into the dried ceramic mold after the model is removed. A positive aspect of this process is the precipitation of disperse particles of salt from the solution in the pores of the ceramic as it is being dried. The least expensive salts are barium and calcium chlorides. This method is not widely used because an optimal method of permeation is not available. The main difficulty is the question of thermal stability of the salts on contact with the vacuum-poured alloy. If the salt was not oxidized during firing, its sublimation from the surface of the ceramic gives rise to nonmetallic inclusions on the surface of the cast part.

Barium chloride melts at 1234 K [2], which is higher than the firing temperature of the mold, and it practically does not oxidize at 1173 K [3]. At atmospheric pressure it boils above the pouring temperature of some alloys. Calcium chloride melts at 1053 K and boils at 1873 K. Appreciable decomposition of $CaCl_2$ in air starts at 1103 K and in the presence of SiO_2 above 993 K and in the presence of Al_2O_3 above 1073 K via the reaction [4]

$$2CaCl_2 + SiO_2 + O_2 = 2CaO \cdot SiO_2 + 2Cl_2.$$

The reaction leading to the formation of barium silicate follows the same scheme. Since $CaCl_2$ at the firing temperature of the ceramic is in the liquid state, it can be more effective because it spreads and fills micropores and macrocracks. Thus, the ceramic can be strengthened by the formation of strong barium and calcium silicates in its pores. The activity of the silica decreases in parallel as a result of its being transferred into a compound. However, at high $CaCl_2$ concentration, as a result of the filling of molds heated to temperature 1173 K, the salt melt can appear on the surface of the ceramic in contact with the poured metallic melt.

In [5] it is proposed that a ceramic mold be permeated with 15 – 35% water solutions of $CaCl_2$ to increase strength. The permeation time and the strengthening of the ceramic are not indicated. In [6] it is shown that the formation of a continuous film on the surface of cold molds is accomplished by permeation of 24 – 36% solutions of $BaCl_2$ or $CaCl_2$.

The absence of a salt film on the surface of the ceramic is attained by means of two parameters: salt concentration and permeation time. To determine the permeation effectiveness the mass content of salts was lowered to 5 and 10% and the permeation time was regulated. Standard five- and nine-layer corundum-sillimanite samples were fabricated [7]. This choice is made because the specific load σ_b for the thicker samples must be lower. The mass content of silica at GRÉ Company was 16.8%. After the model was dissolved and the ceramic mold washed the mold was dried at temperature 473 K and immersed in the corresponding solutions for 5 sec. After drying the ceramic samples were separated from one another and fired at temperature 1223 K for 5 h. The heated samples were quickly transferred into a furnace at temperature 1173 K, in which the standard three-point failure apparatus was inserted, and the strength in bending was determined (Table 1).

TABLE 1. The Strength σ_b of Corundum-Sillimanite Ceramic at 1173 K

No.	Sample thickness, 10^{-2} m	Salt content melt, wt.%	Strength σ_b, MPa
1	0.58 – 0.65	No treatment	3.59
2	0.48 – 0.59	5 $BaCl_2$	4.59
3	0.95 – 1.00	5 $BaCl_2$	4.24
4	0.45 – 0.50	10 $BaCl_2$	5.13
5	0.48 – 0.52	5 $CaCl_2$	4.21
6	0.52 – 0.60	10 $CaCl_2$	5.18

The results presented in Table 1 showed that short-time treatment of ceramic with a salt solution increases the strength of the ceramic by more than 18%. However, separation of thin refractory particles from its surface is noticeable after permeation of 5% solutions (variants 2, 3 and 5) and firing. This occurred because of partial breakdown of the binder on the surface of the ceramic as a result of repeated immersion into water, while a low concentration of the hardening material did not permit compensating this softening. It is evident that this guarantees the absence of salt on the surface of the mold. When the salt concentration is increased to 10% individual particles may not react fully.

At temperature 1198 K and higher the barium chloride lattice transforms from the α- into the β-modification, whose melting and boiling temperatures are 1234 K and 2310 K, respectively [2]. The restructuring of the barium chloride lattice should increase the intensity of its solid-phase sintering with the ceramic. For this reason the firing of the ceramic should be done at 1223 K.

The present authors investigated the possibility of oxidation of salts at temperature 1223 K. The salts were placed into a SNOL 2.2,5.2/12,5–I1 chamber furnace with an electronic temperature regulator and held for 0.1 – 1.0 h. Next, a water solution with salt content 5 wt.% was prepared with weighed amounts of 2.5 g on analytical scales to within ±0.1 mg. The acidity of the solution was measured by the standard procedure. The degree of conversion of the salt was calculated by the method of [8]. Soaking $BaCl_2$ for 1 h increased the pH from 6.048 to 10.248, while the degree of conversion was only 2.8%; the conversion rate was 0.1 %/min in the last 10 min and 0.2 – 0.3 %/min over the preceding time segment. Thus, at the mold firing stage $BaCl_2$ oxidizes very little. At temperature 1873 K the vapor pressure above BaO is higher than in silica [9], reaching the va-

cuum level in the pouring zone. However, this oxide practically does not dissociate: its degree of dissociation is 0.066 – 0.220% at temperatures 1500 – 1873 K, and the main component with dissociation of silica is the chemically active monoxide SiO. The molecular oxygen pressure at temperature 1773 K as a result of the dissociation of silica is higher than in the case with BaO, taking the values log $P = -7.39$ and –8.15, respectively [9]. Taking into account the fact that barium oxide passes through the solid-phase sintering stage in the ceramic mold, its chemical activity decreases. In [3] it is shown experimentally that barium chloride is most stable against sublimation. The post-firing pH of $CaCl_2$ increased less, to 9.430, and the degree of conversion was less than 2%.

The use of this method is fully possible with open melting as well as with a low vacuum in the pouring zone.

Knowledge of all particulars and structure of the formation of ceramic makes it possible to determine the most effective strengthening mechanism and to make a technological decision concerning the development of a high-quality ceramic mold taking account of the alloy pouring conditions.

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